U.S. Army Research, Development and Engineering Command

Energy-Storing Structures: Composite Capacitors and Batteries

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

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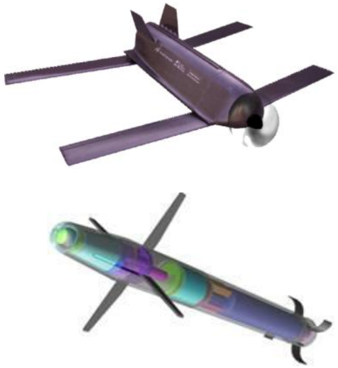
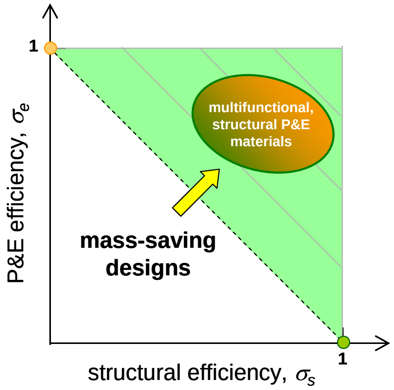
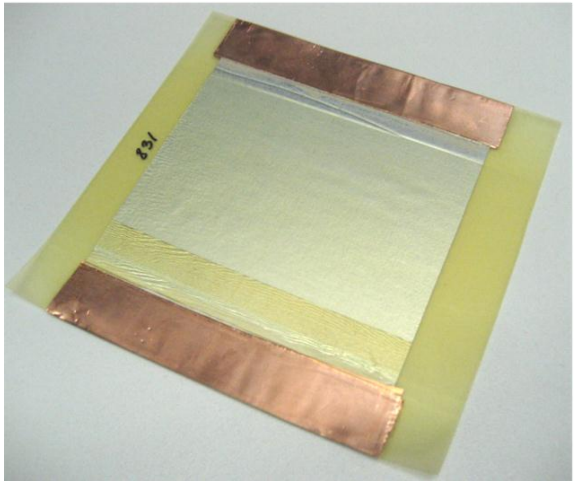
Outline

Motivation and Approach

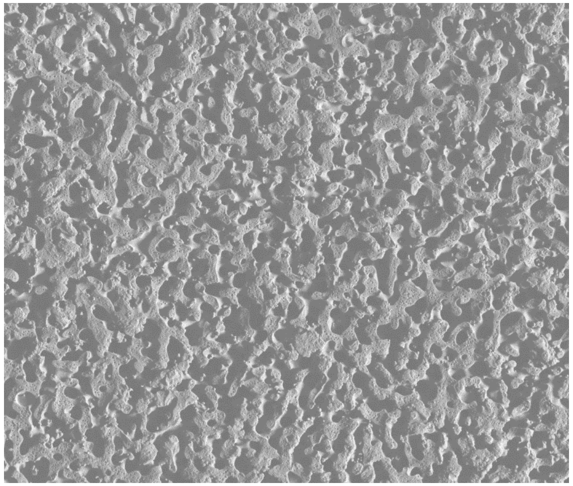




Structural Capacitors



Structural Batteries



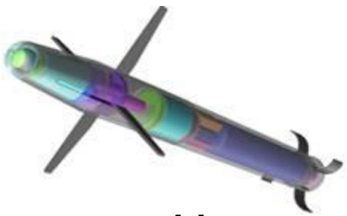
ARL research team: Eric Wetzel Jim Snyder, Danny O'Brien, Dan Baechle, Eddie Geinger, Oleg Yurchak, Wai Chin, Kris Behler

U.S. Army Power and Energy

Batteries

UAV propulsion

night vision
goggles, radios



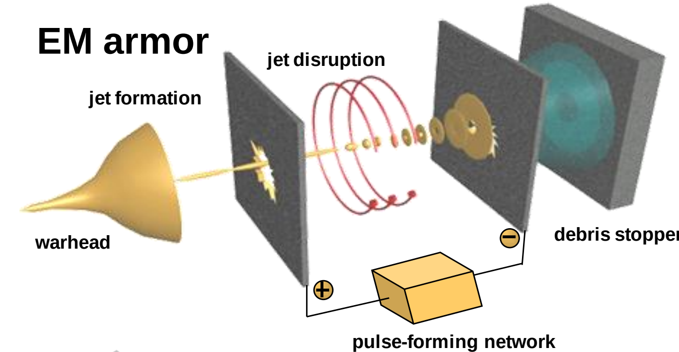
smart munition sensing,
control, computation

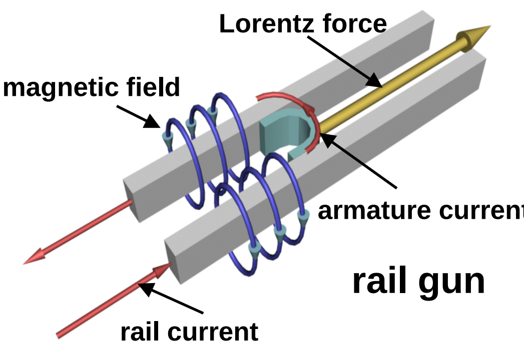
hybrid electic-
combustion
powerplants

Capacitors

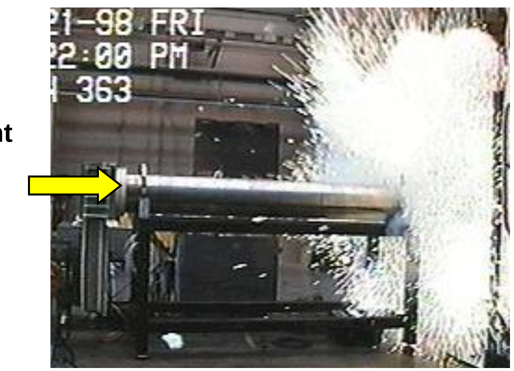
pulsed power applications

EM armor





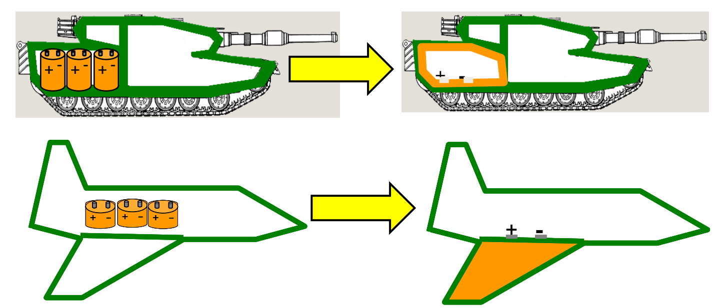
rail gun



Objective

Reduce system mass (or volume) by creating batteries and capacitors that can carry mechanical loads.

Batteries / capacitors serve as structural or armor elements.



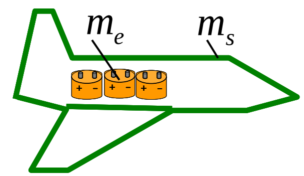
Mass Savings through Multifunctionality

$\sigma_e \rightarrow$ mass-normalized P&E efficiency
$\sigma_s \rightarrow$ mass-normalized structural efficiency

$$\sigma_e = \frac{\overline{E}_{se}}{\overline{E}_e}$$

$$\sigma_s = \frac{\overline{S}_{se}}{\overline{S}_s}$$

Conventional design



$$\boxed{M = m_s + m_e}$$

system mass [kg]
structure mass [kg]
P&E mass [kg]

Multifunctional design

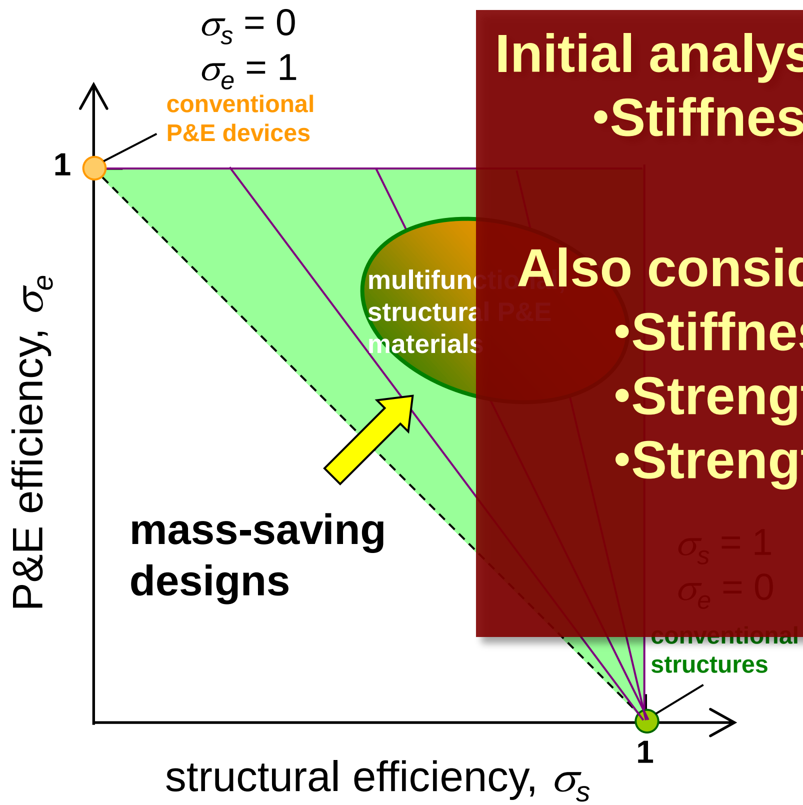
$$\boxed{M^* = m_s^* + m_e^* + m_{se}^*}$$

structural P&E mass [kg]

$$= \left(m_s - \sigma_s m_{se}^*\right) + \left(m_e - \sigma_e m_{se}^*\right) + m_{se}^*$$

$$= \left(m_s + m_e\right) + \left(1 - \sigma_s - \sigma_e\right) m_{se}^*$$

$$\left(M - M^*\right) = \left(\sigma_s + \sigma_e - 1\right) m_{se}^*$$



Initial analysis driven by:
- **Stiffness / Mass**

Also consider:
- **Stiffness / Volume**
- **Strength / Mass**
- **Strength / Volume**

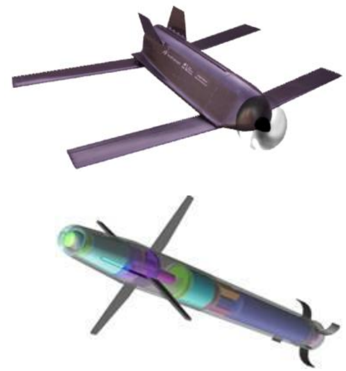
mass-savings can be achieved if:

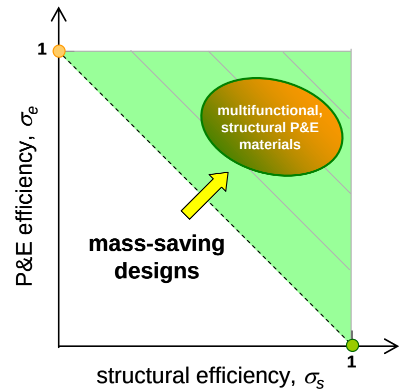
$$\boxed{\sigma_{mf} \equiv \sigma_e + \sigma_s > 1}$$

Mass savings possible even if multifunctional material performs individual functions less efficiently than monofunctional materials.

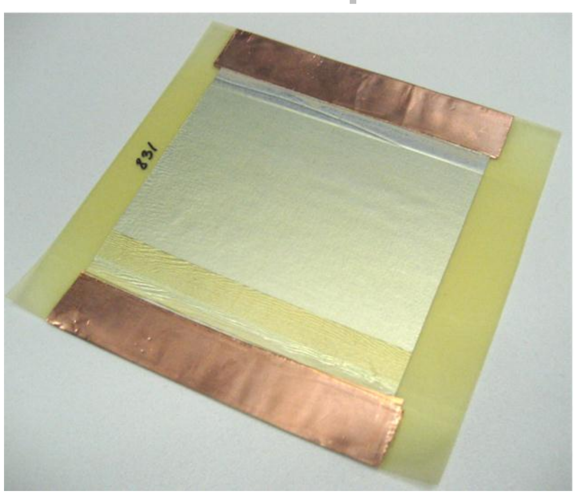
Outline

Motivation and Approach

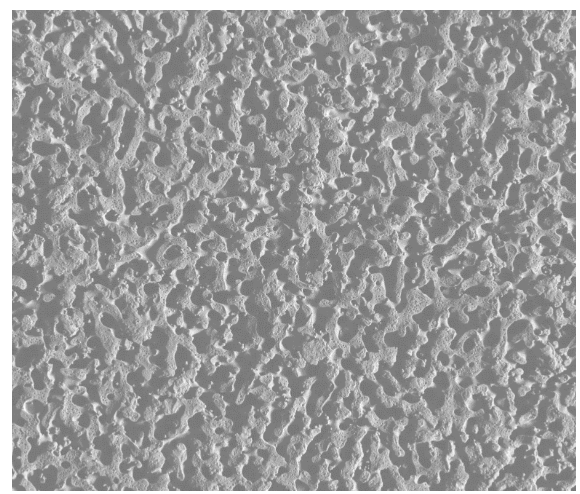




Structural Capacitors

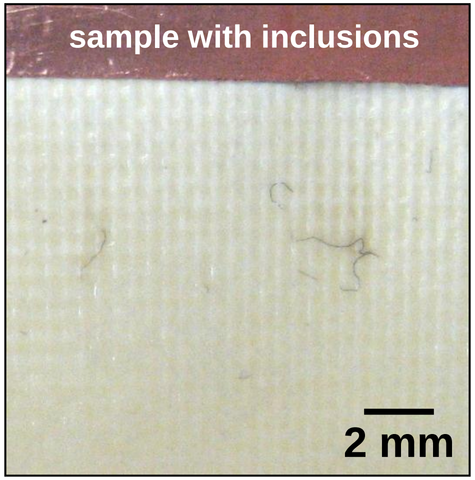


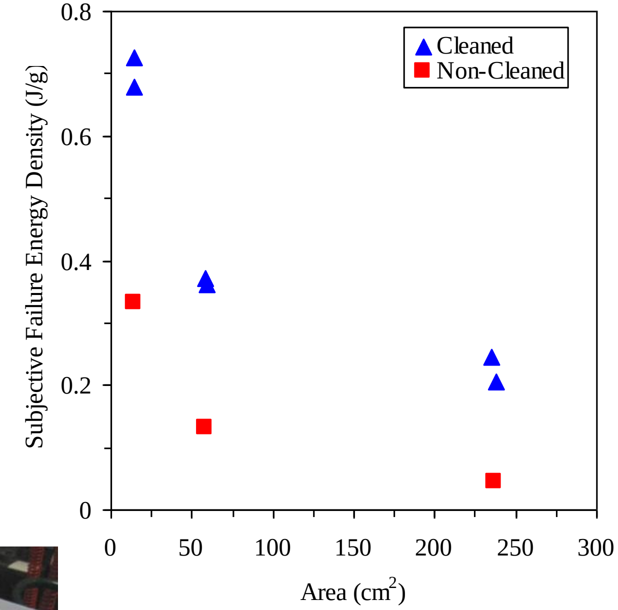
Structural Batteries



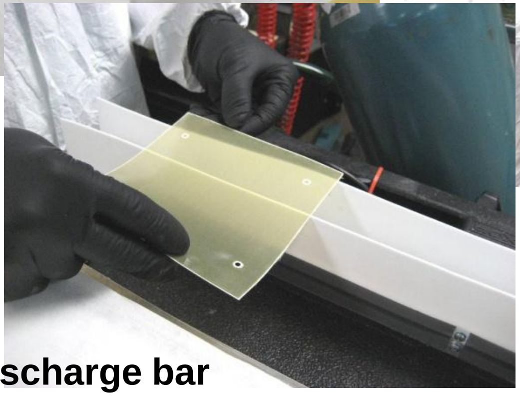
Clean Processing Required

laminar flow room





solvent wipe

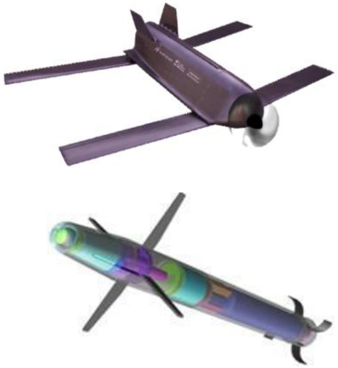


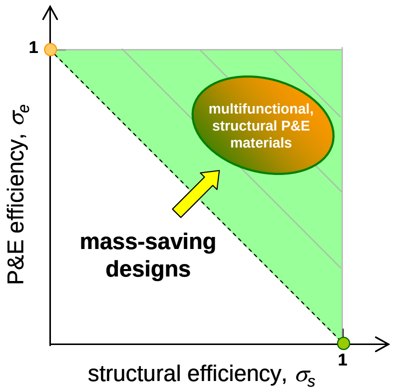
static discharge bar

dry nitrogen

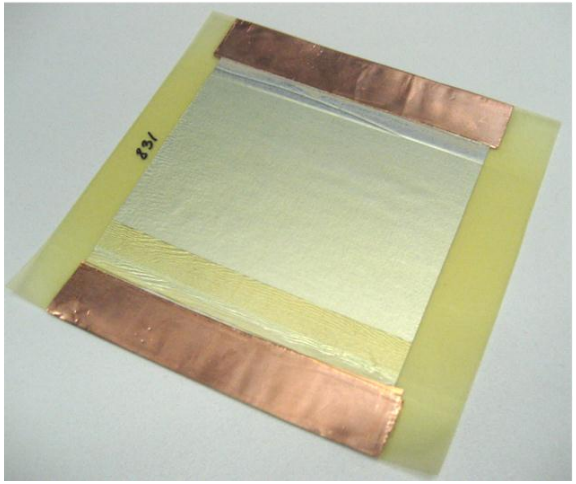
Outline

Motivation and Approach

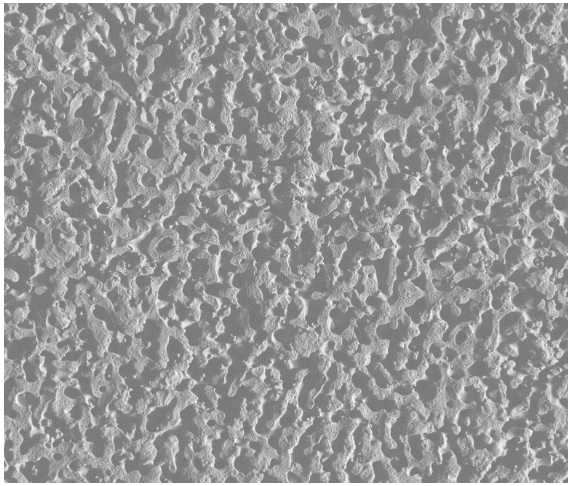




Structural Capacitors



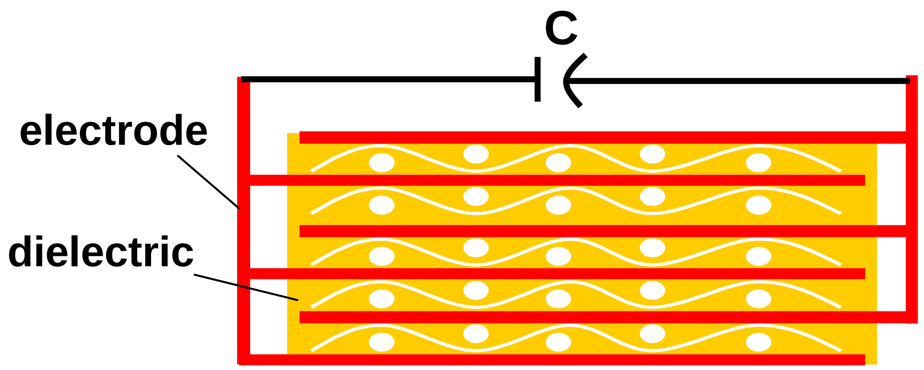
Structural Batteries

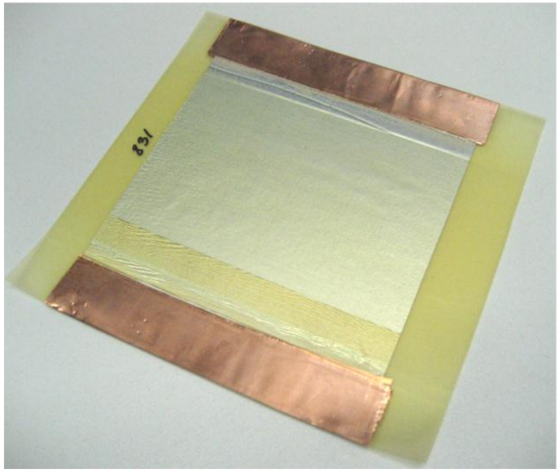


Anatomy of a Structural Capacitor

Electrodes
- Metallized films and papers
- Examples: 100 nm Al on Kapton film, 20 nm Al on Kraft paper

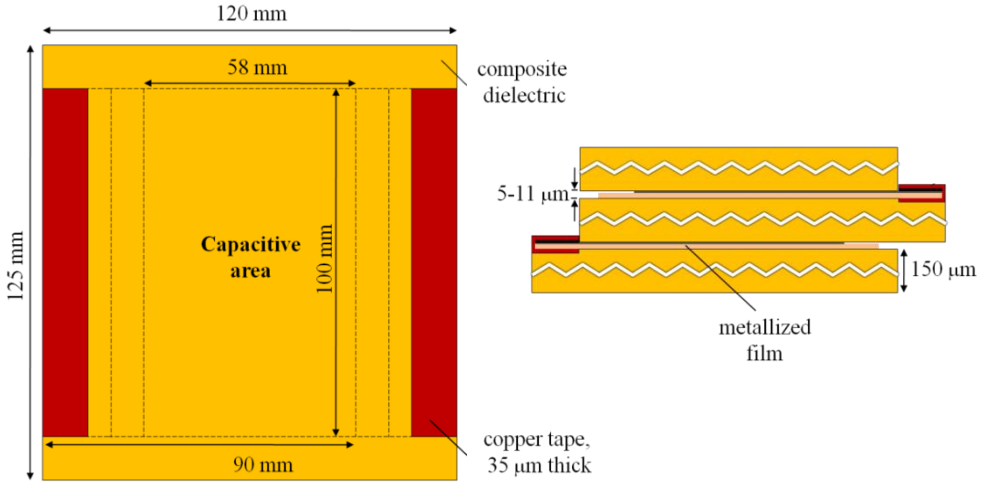
Composite dielectric
- Glass fiber-reinforced polymers
- Example: Nelcote printed circuit board (PCB) prepreg



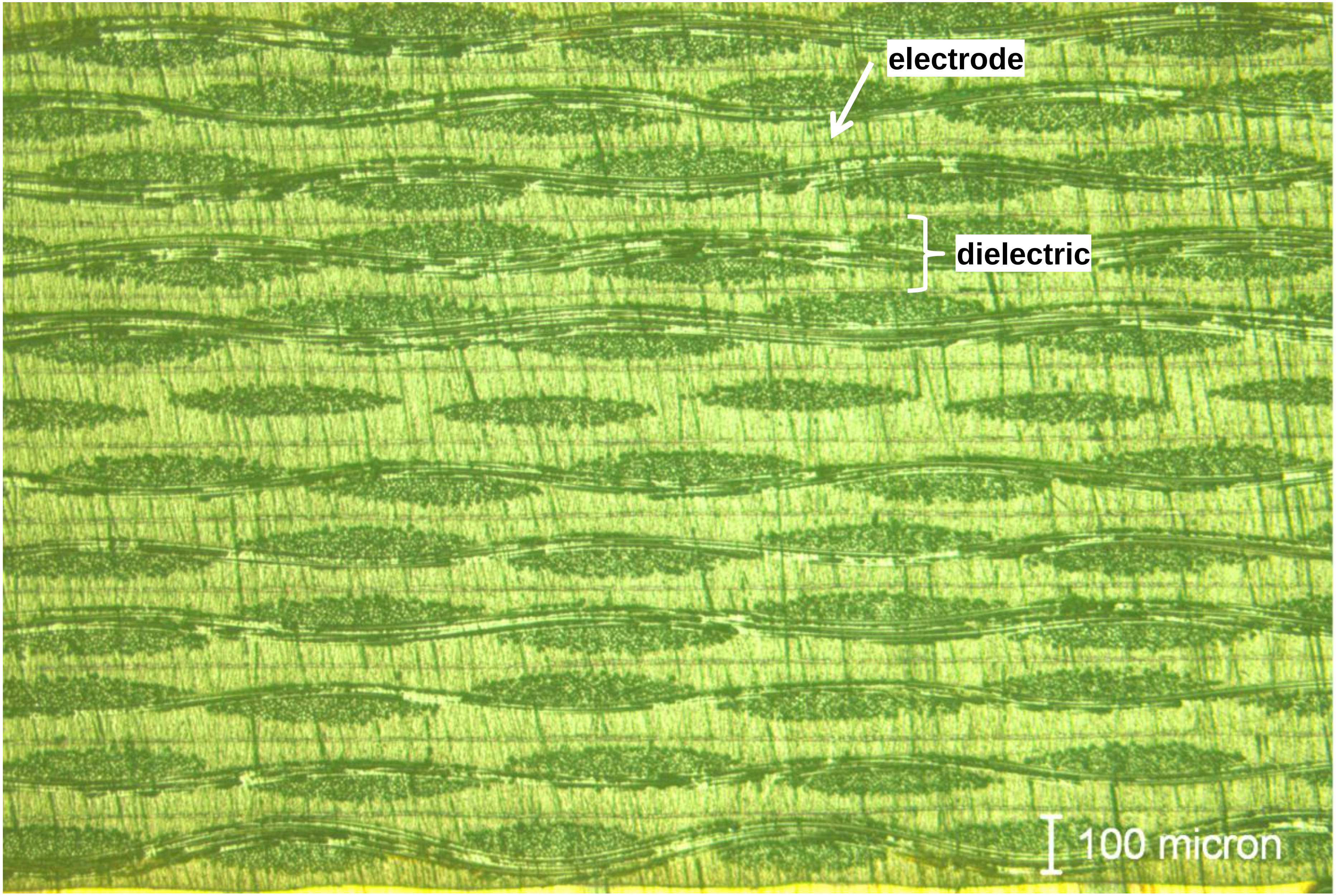


Autoclave-processed structural capacitor

- **Objective: High energy density, scalable structural capacitor**
  - High energy density
    - Vanishingly thin electrodes
    - Low void content
  - Scaling
    - Clean processing
    - Self-clearing electrodes
    - Scalable assembly

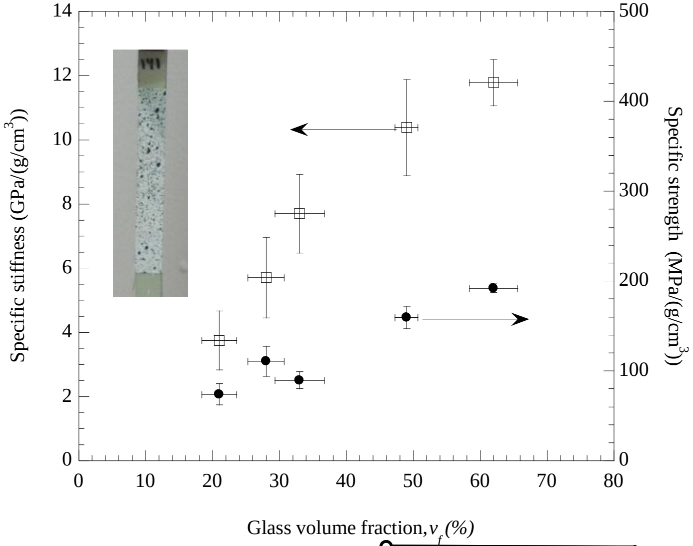


Cross-Section of Structural Capacitor

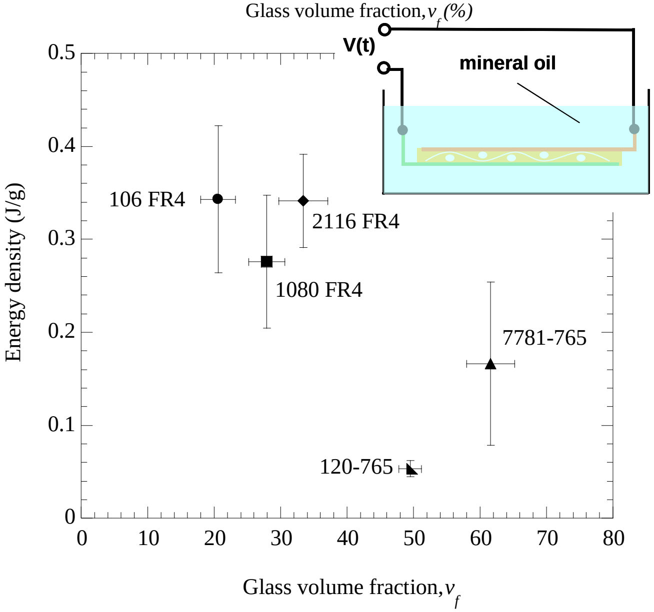


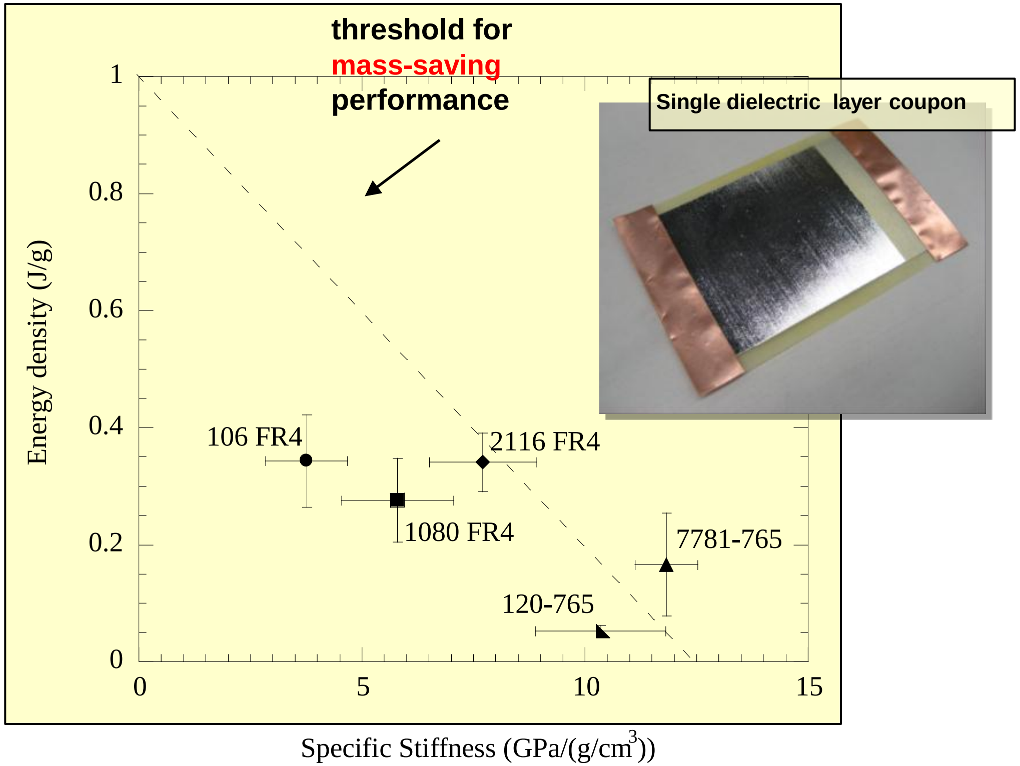
Coupon Level Experiments
Fiber Volume Fraction Effects

Fiber volume fraction study showed that good multifunctional performance is obtained at high fiber volume fractions.



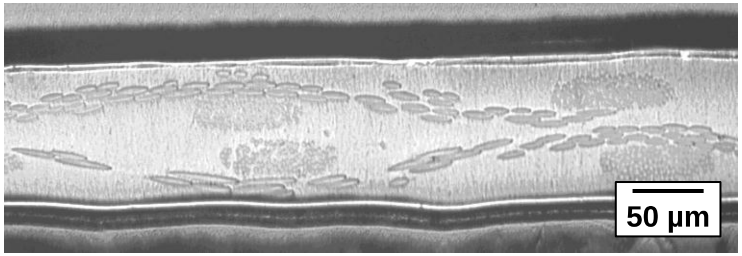
Group	Fabric type	Matrix type	Weave type	Fabric thickness (mm)	Areal density (g/m^2)
1	106	FR4 (PCB)	Plain	0.04	25
2	1080	FR4 (PCB)	Plain	0.06	49
3	2116	FR4 (PCB)	Plain	0.10	109
4	120	765 (struct)	4H Satin	0.09	107
5	7781	765 (struct)	8H Satin	0.22	299

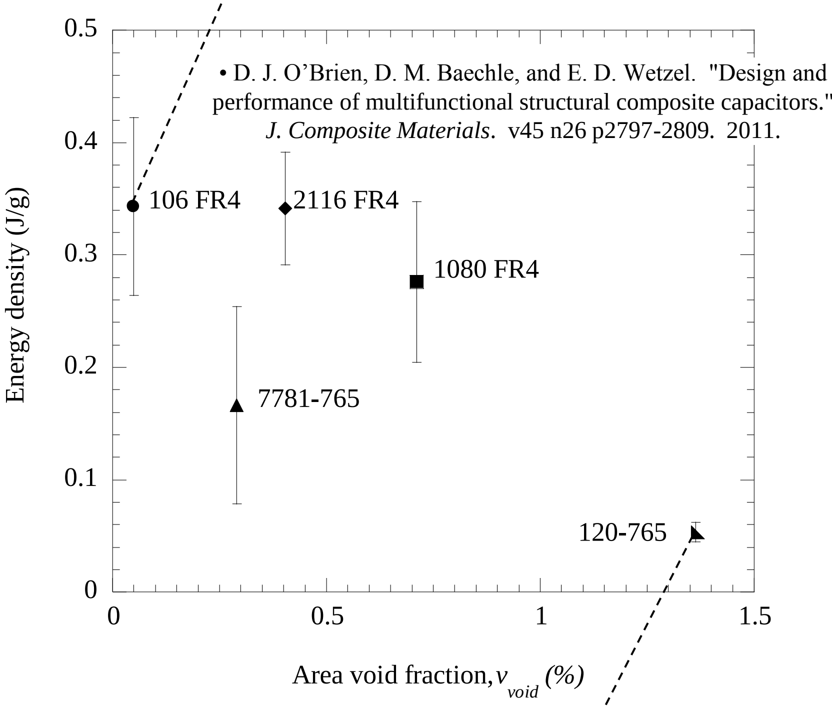


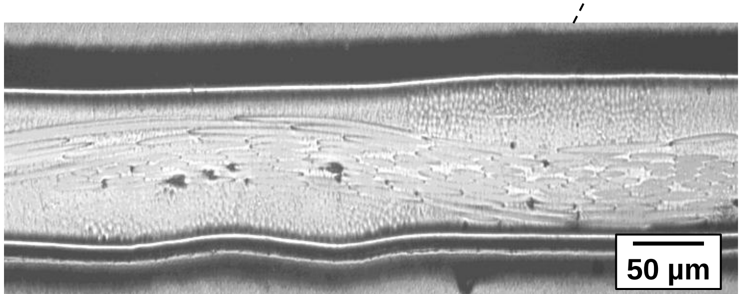


O'Brien et al. *J Comp Mat.*, 45(26) 2011.

Void Fraction Effects

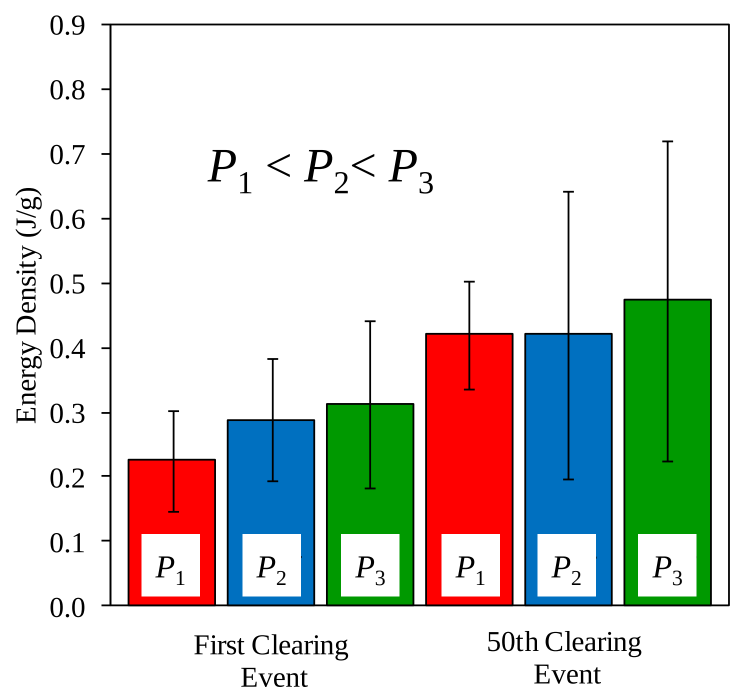






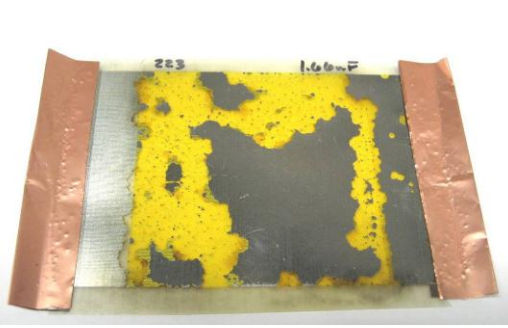
- **Energy density decreases with increasing void fraction**
  - **Voids concentrate electric fields and reduce local dielectric strength**

- **Processing needs to be optimized to minimize void generation, growth, and persistence**
  - **High pressure processing**
  - **Minimize volatilization**

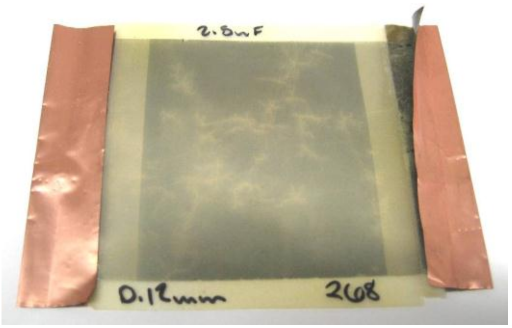


Electrode Selection and Performance

Self-clearing electrodes to enhance flaw tolerance

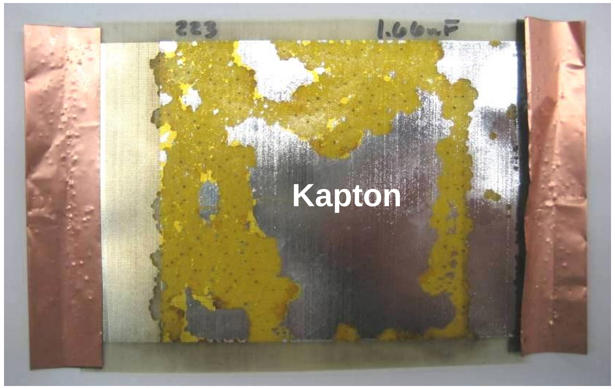


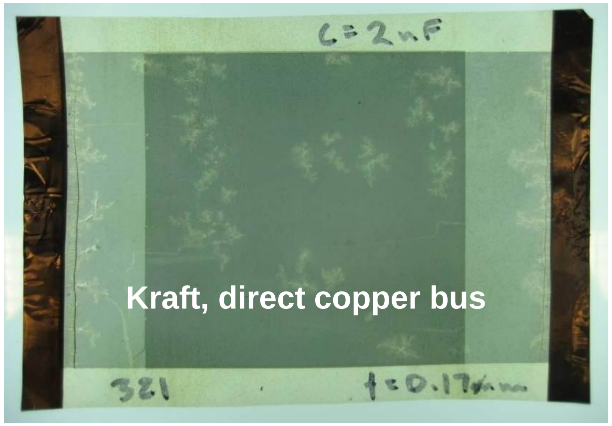
Kapton electrode



Kraft paper electrode

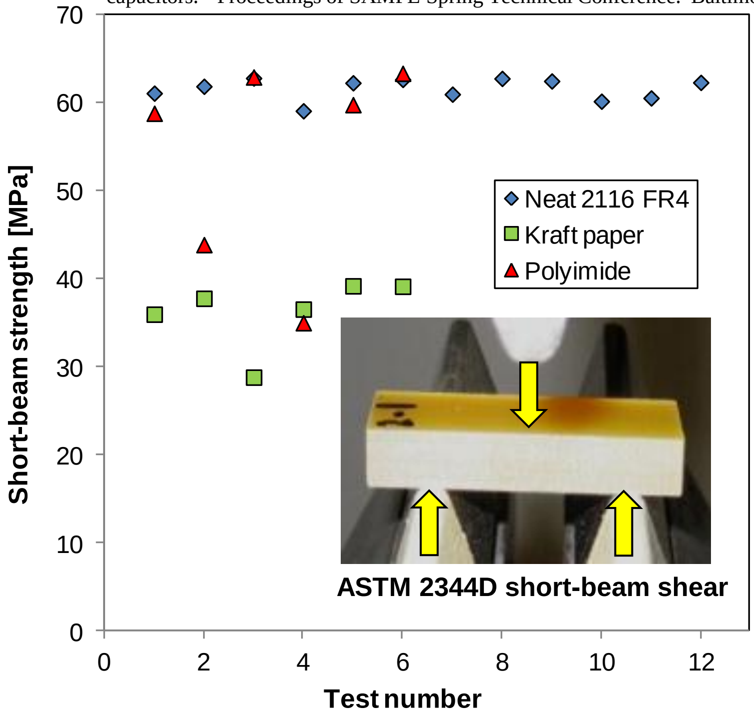
Electrode connectorization

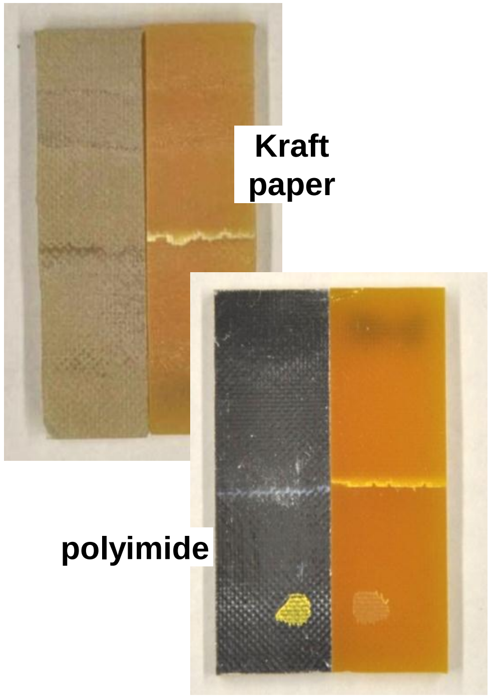




Mechanical performance

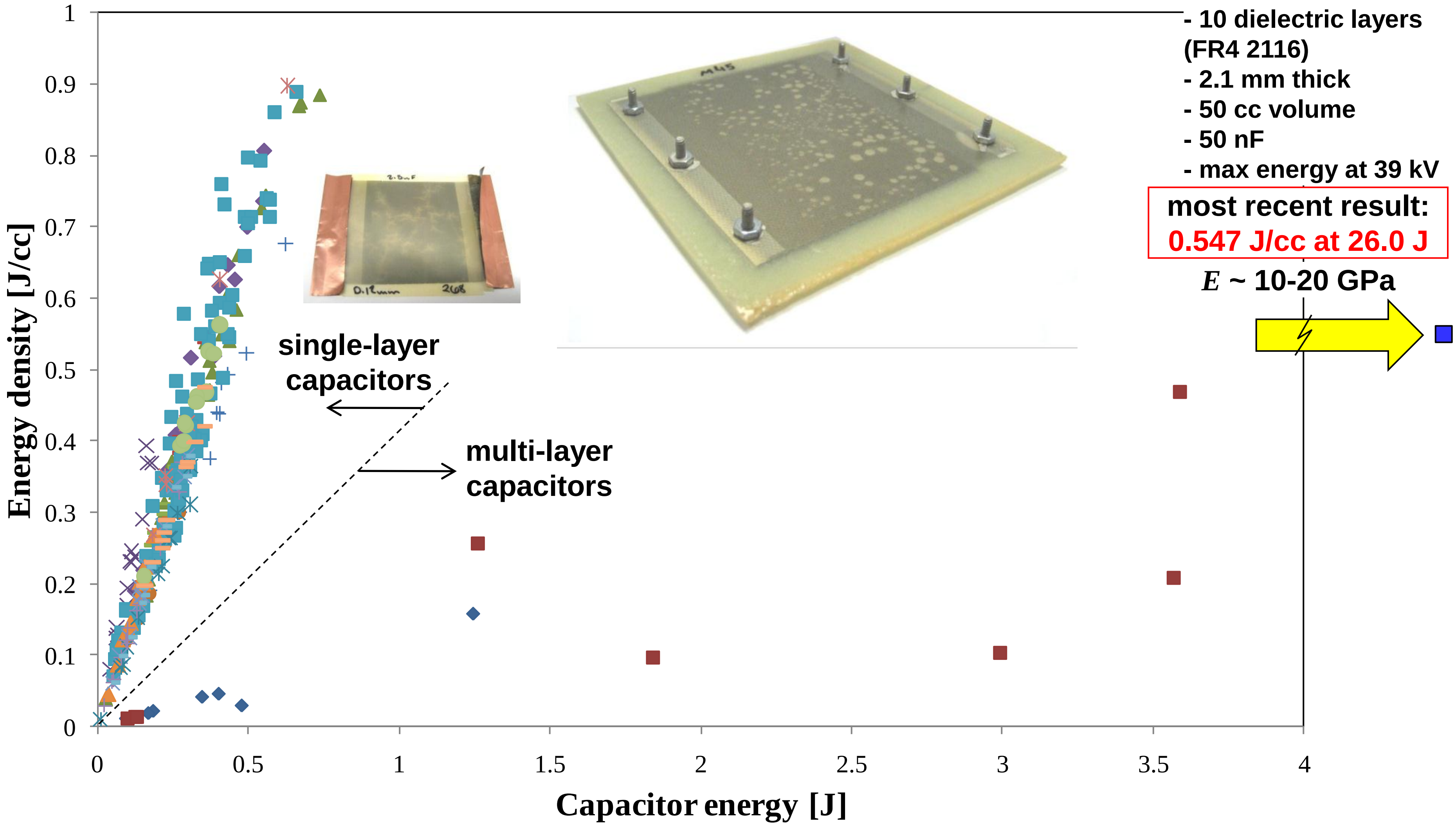
- O.B. Yurchak, D. J. O'Brien, D. M. Baechle, and E. D. Wetzel. "Shear properties of multifunctional structural capacitors." Proceedings of SAMPE Spring Technical Conference. Baltimore, MD. May 21-24, 2012.





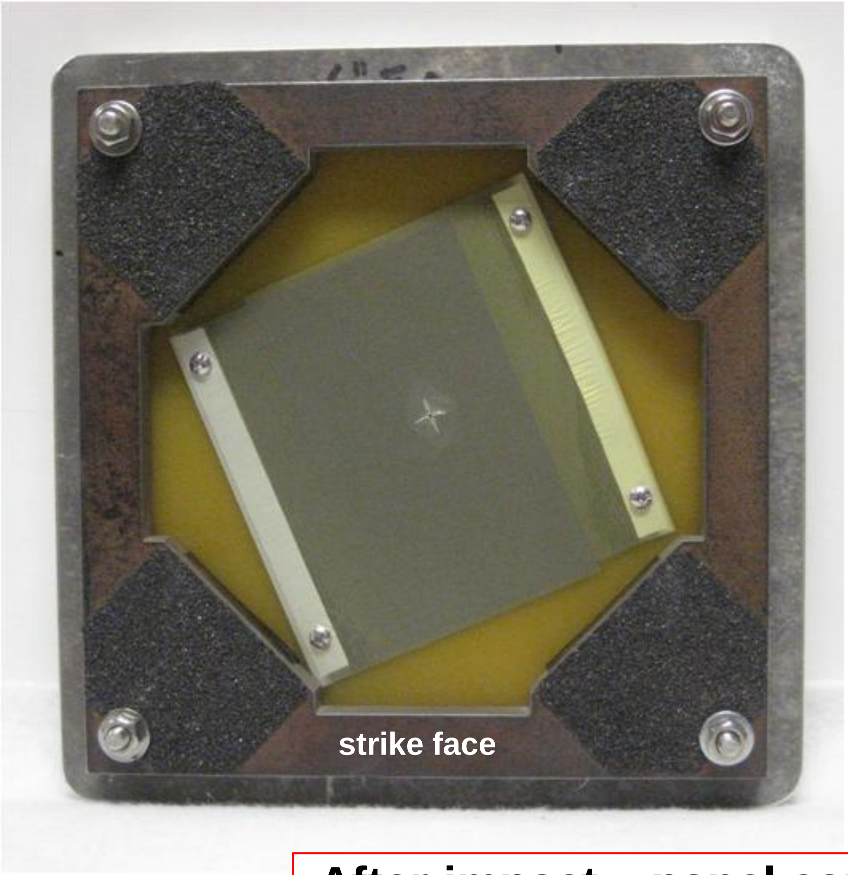
Scaled Assembly and Performance

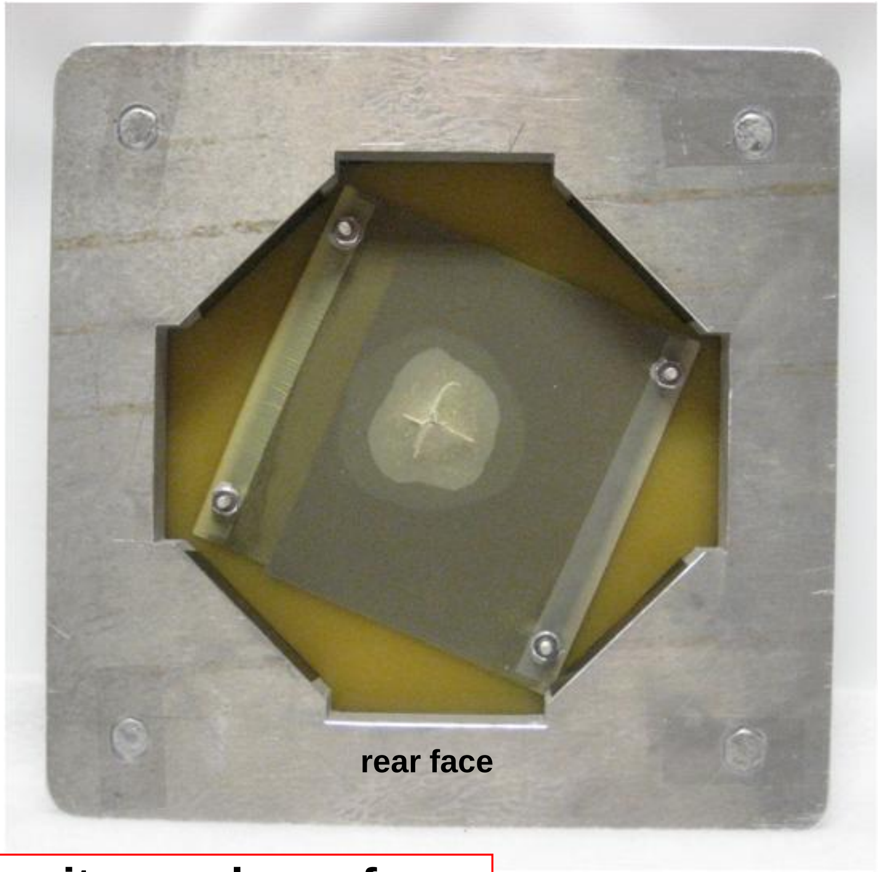
- Developed scalable assembly technique for efficient stacking of many (dozens) electrode, dielectric, and bus layers
- Maintaining excellent energy density up to high energies (volume)



Impact Performance of Structural Capacitors

- Ballistically impact 4-dielectic layer, FR4-2116 composite panel while energized at 15 kV
  - 203 x 203 x 2 mm panels
  - Impacted with 0.22 cal steel sphere at 667 fps (penetration)

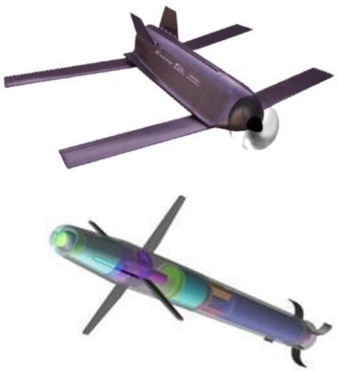


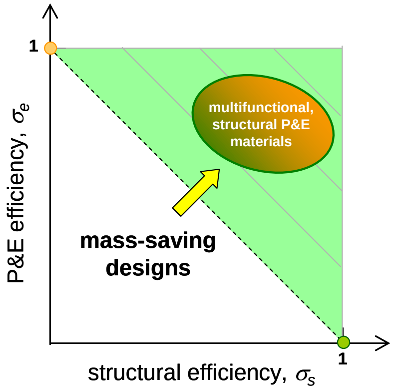


After impact... panel capacitance drops from 16.7 nF to 13.5 nF, but still holds 15 kV.

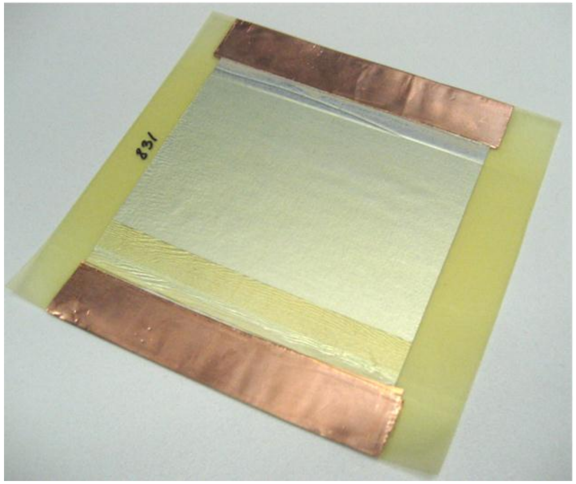
Outline

Motivation and Approach

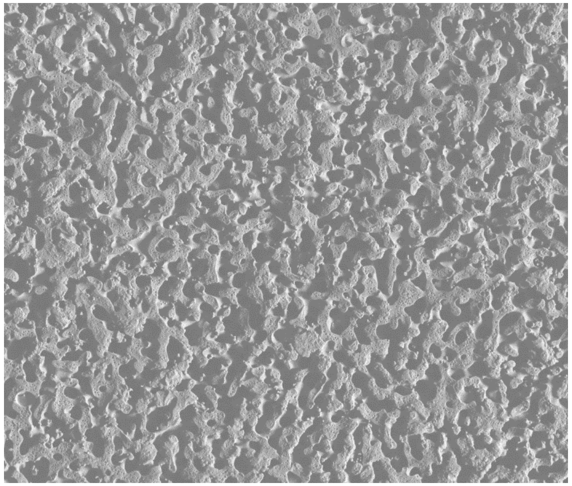




Structural Capacitors



Structural Batteries



Anatomy of a Structural Battery

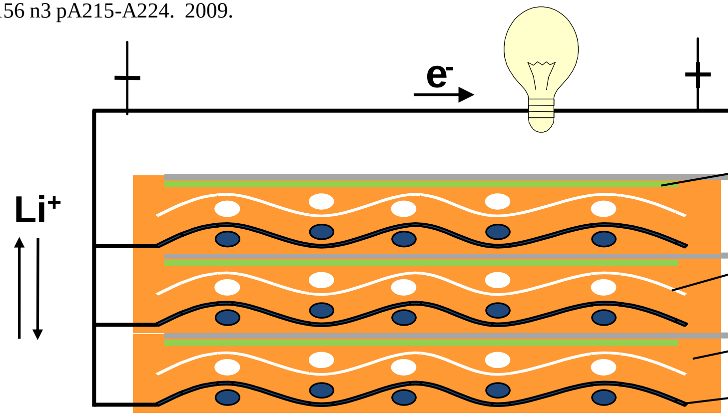
Anodes

- Intercalates Li ions and provides structural reinforcement
- Example: T-300 PAN-based carbon fiber fabric

J. F. Snyder, E. L. Wong, and C. W. Hubbard. "Evaluation of commercially available carbon fibers, fabrics, and papers for potential use in multifunctional energy storage applications." *J. Electrochem Soc.* v156 n3 pA215-A224. 2009.

Separator

- Provides electrical insulation while permeable to electrolyte and ions
- Examples: glass veil cloth, Celgard® porous polypropylene



Cathode

- Comprised of current collector + active cathode material
- Reacts with Li ions, busses electrons, and provides structural reinforcement
- Example: Perforated stainless steel foil coated with $LiFePO_4$ + acetylene black + binder

Electrolyte

- Solid polymer electrolyte → provides balance of mechanical properties and ion conductivity

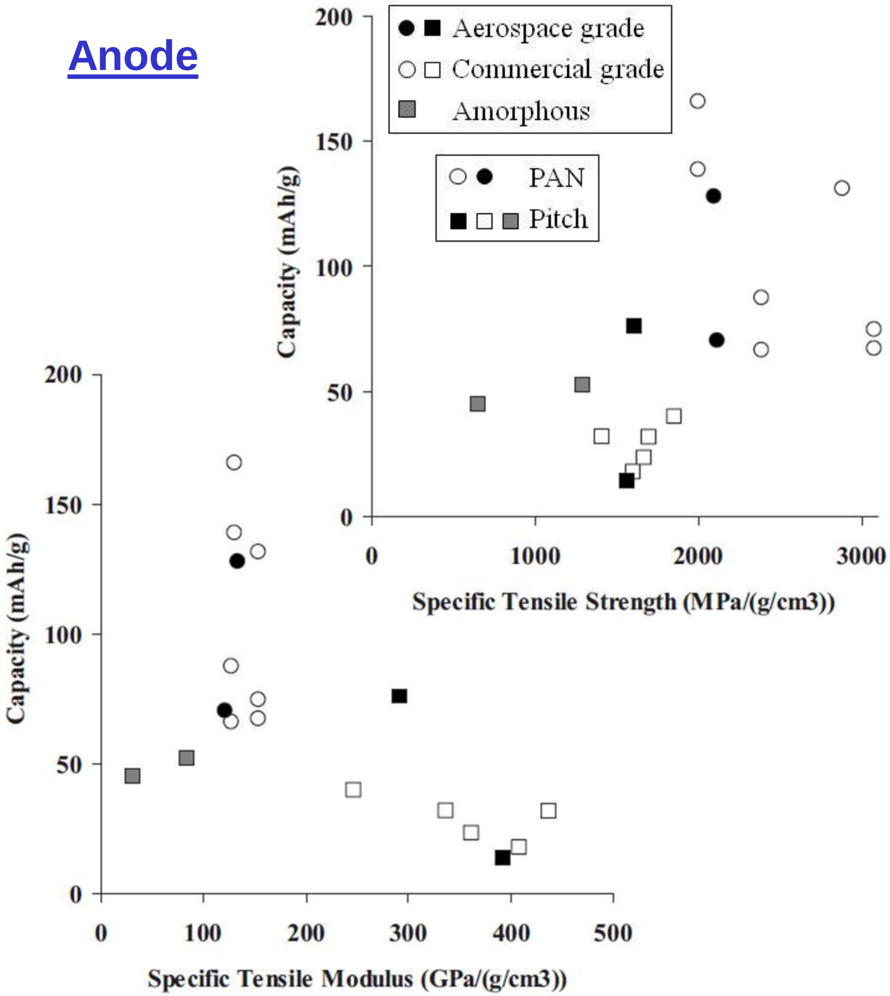
Most critical technical / scientific challenge

• E.B. Gienger, J.F. Snyder, E.D. Wetzel, and K. Xu. "Multifunctional structural composite supercapacitor development and evaluation." Proceedings of SAMPE Spring Technical Conference. Baltimore, MD. May 21-24, 2012.

(these electrolytes are also needed for structural supercapacitors)

Anode and Cathode Design

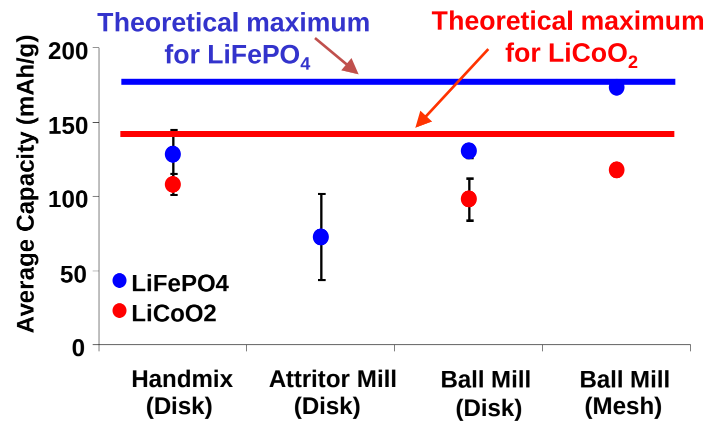
Anode

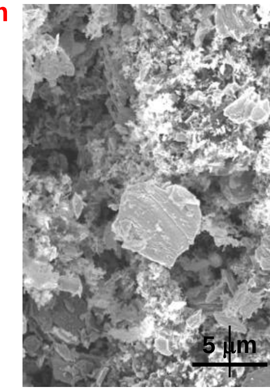


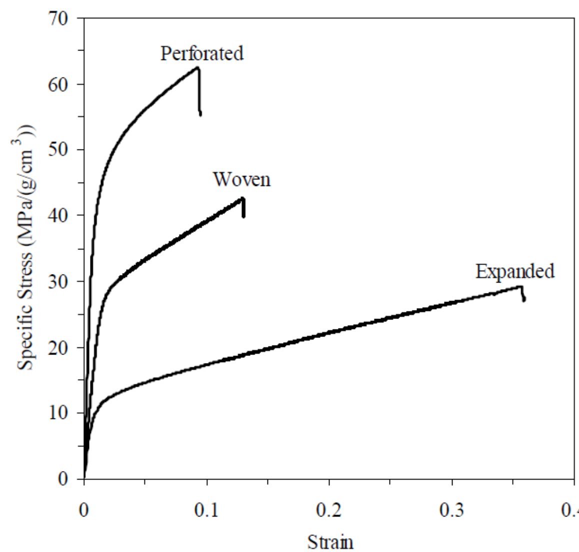
Traditional structural carbon fiber reinforcement should provide excellent anodic functionality.

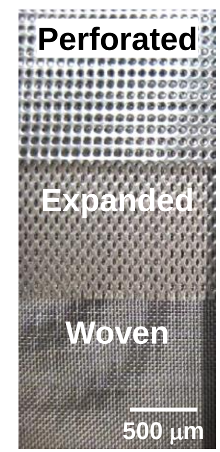
J. F. Snyder, E. L. Wong, and C. W. Hubbard. "Evaluation of commercially available carbon fibers, fabrics, and papers for potential use in multifunctional energy storage applications." *J. Electrochem Soc*. v156 n3 pA215-A224. 2009.

Cathode









Cathode and current collector components provide good performance… but challenging to integrate.

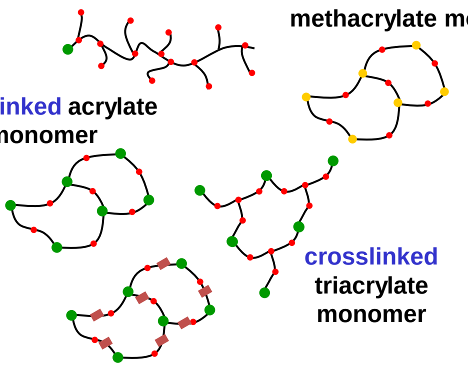
Structural Electrolyte Architectures

Homopolymers

comb monomer

crosslinked methacrylate monomer

crosslinked acrylate monomer

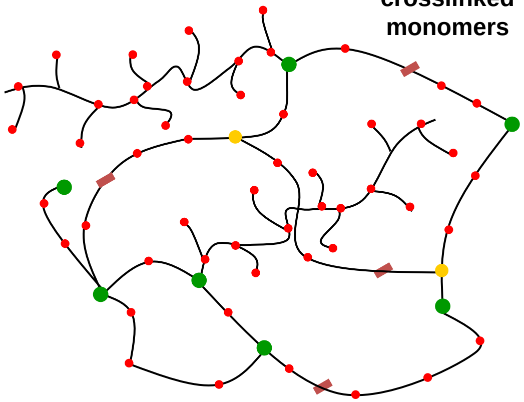


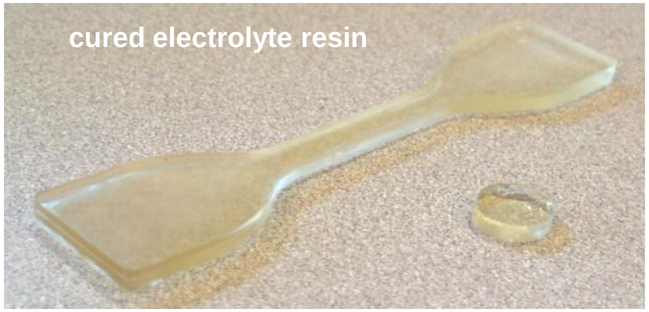
crosslinked triacrylate monomer

crosslinked monomer with additional backbone functional groups

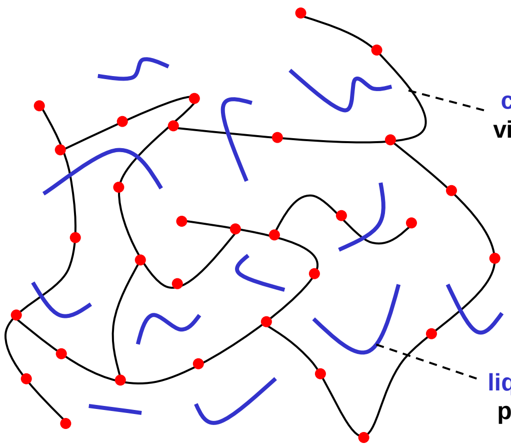
Copolymers

copolymer of comb monomers and crosslinked monomers





Gels



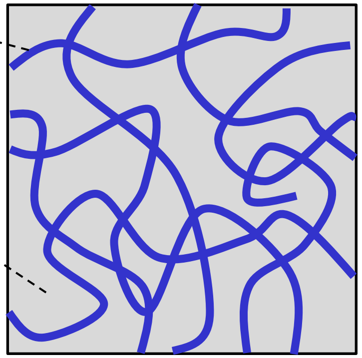
crosslinked vinyl ester or epoxy

liquid (PEG) plasticizer

Micro-foams

liquid electrolyte

crosslinked structural polymer



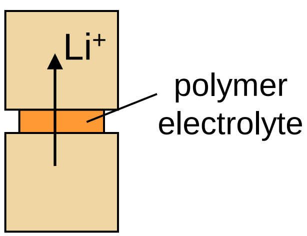
1-100 μm

Multifunctional Properties of Homopolymer / Copolymer Electrolytes

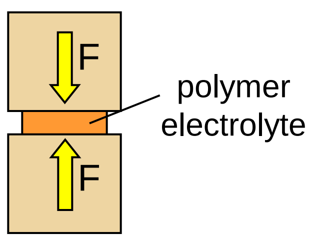
• J. F. Snyder, R. H. Carter, E. D. Wetzel. "Electrochemical and mechanical behavior in mechanically robust solid polymer electrolytes for use in multifunctional structural batteries." *Chem. Mater*. v19 n15 p3793-3801. 2007.

• J. F. Snyder, C. Watson, and E. D. Wetzel. "Improving multifunctional behavior in structural electrolytes through copolymerization of structure- and conductivity-promoting monomers." *Polymer*. v50 p4906-4916. 2009.

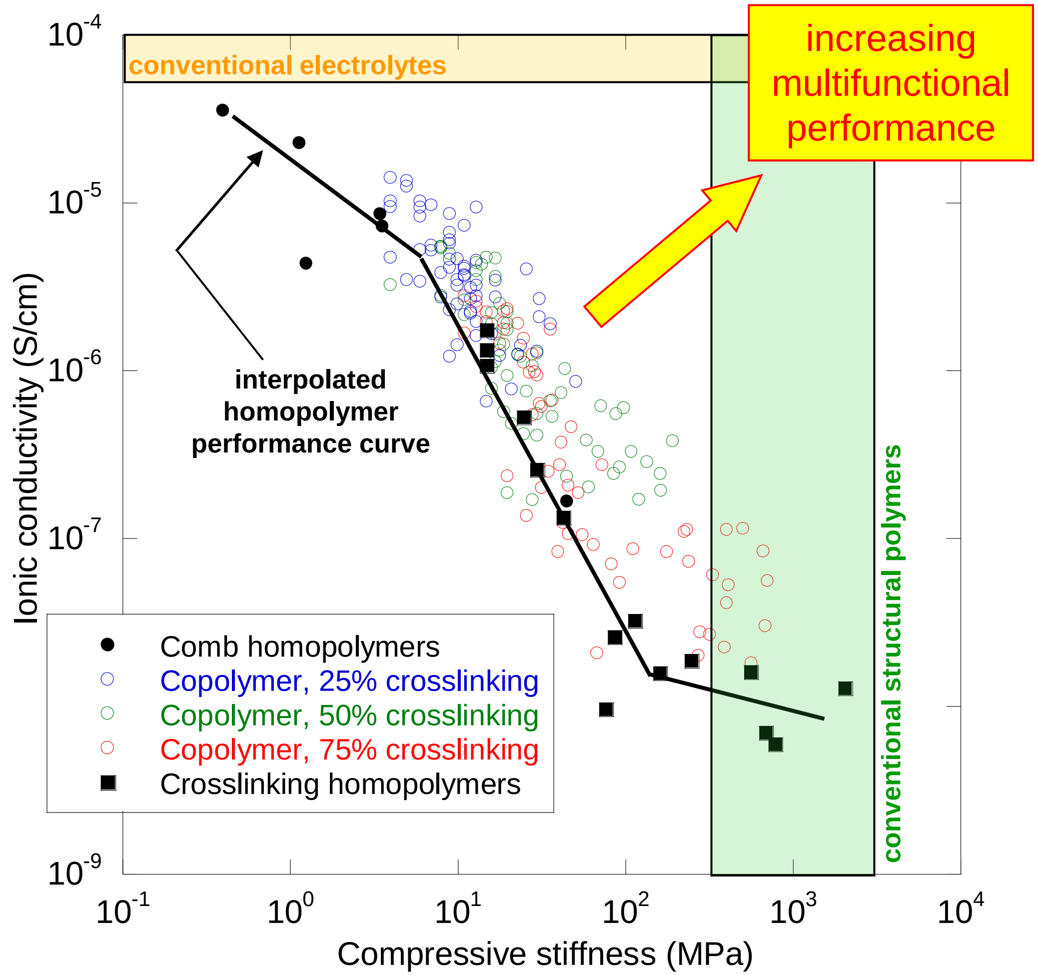
- Vinyl ester backbones
- PEG combs / plasticizers
- Variations in
  - Nature, number of reactive groups
  - PEG length and concentration
  - Endgroups (combs)
  - Crosslinking groups (networks)
- Polymers complexed with lithium triflate for ionic conductivity



Ion conductivity measurement



Compressive stiffness measurement

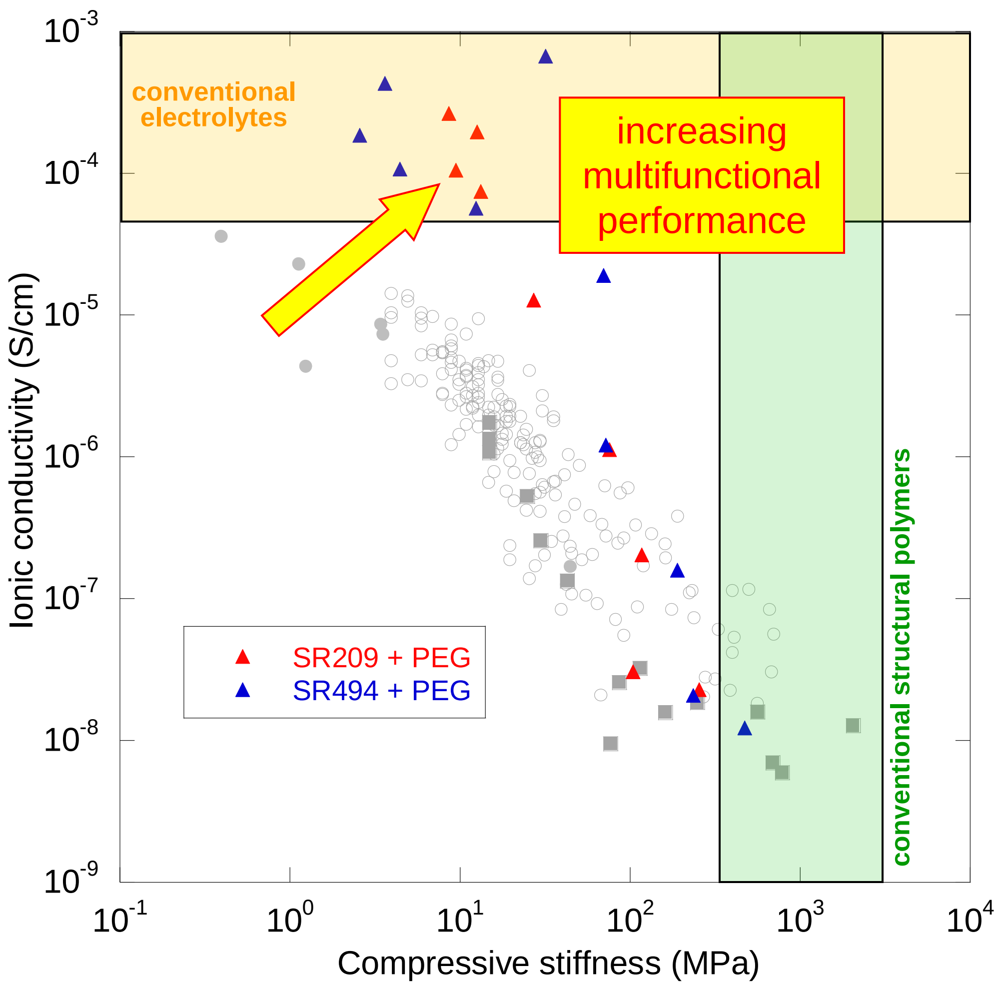


- **Clear inverse correlation between mechanical properties and conductivity**
  - **Copolymers show improved multifunctionality versus homopolymers**

Multifunctional Properties of Gel Electrolytes

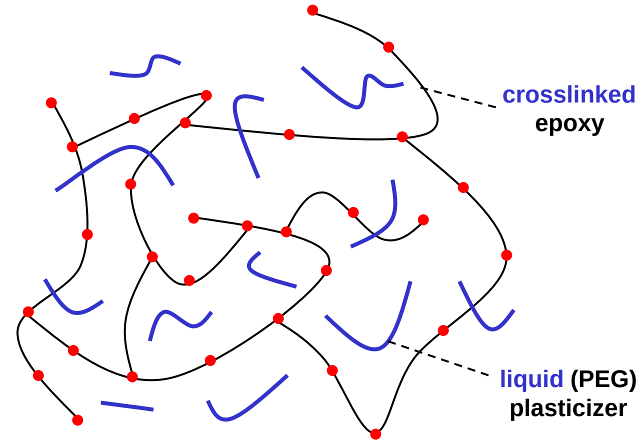
P. T. Nguyen and J. F. Snyder. "Multifunctional properties of structural gel electrolytes." *ECS Transactions.* v11 n32. 2007.

- Gel electrolytes provide greatly **enhanced multifunctional performance**



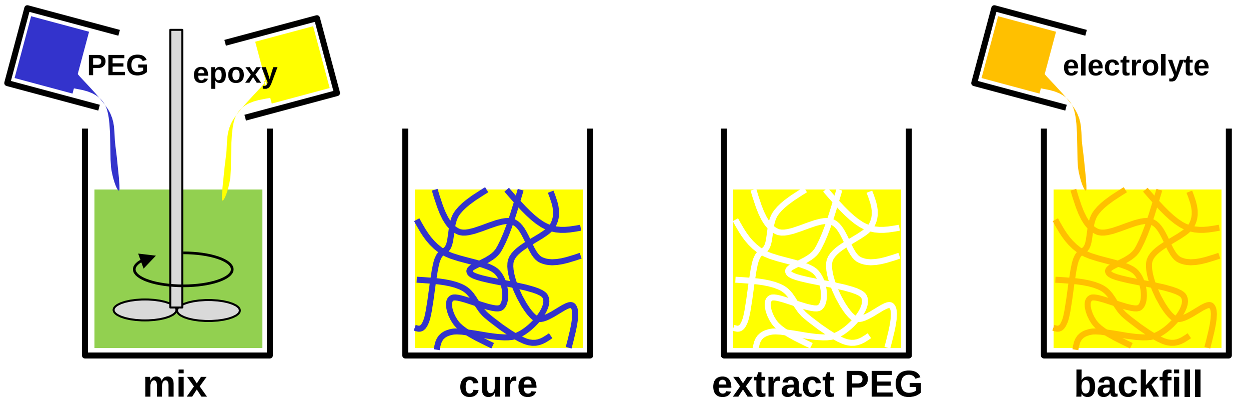
Gel electrolytes provide good balance of mechanical performance and ion conductivity

Example epoxy-based electrolyte:
EPON 828 epoxy plasticized with 80% liquid electrolyte
($C_2HF_6NO_4S_2$ dissolved in 50:50 ethylene carbonate and dimethyl carbonate)



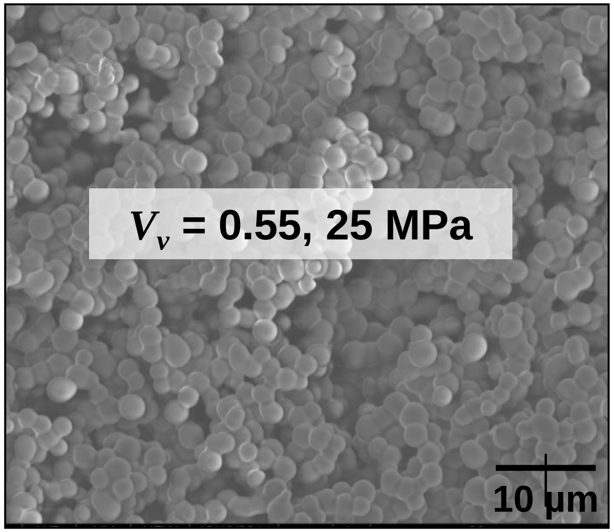
Polymer MicroFoam Electrolytes

- Processing approach
  - PEG (e.g. 70% v/v) mixed with epoxy pre-polymer (e.g. 30%v/v)
  - System cured → phase-separates, leaving micro-sized epoxy/PEG interpenetrating network
  - Sonicate in water, dry in oven to remove PEG
  - Soak in liquid electrolyte to back-fill pores

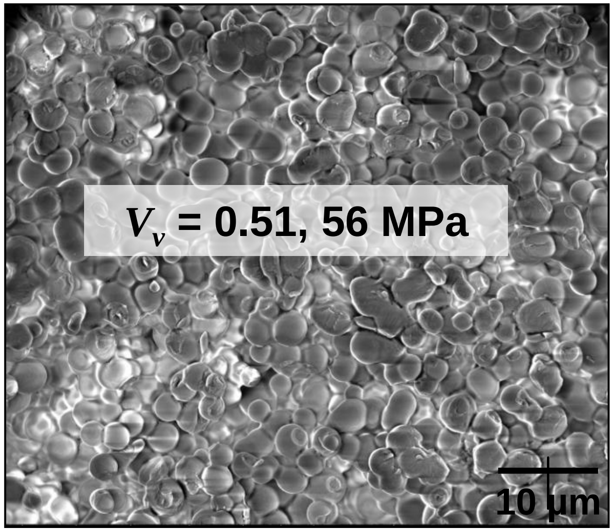


- Tailorable microstructure → PEG/epoxy ratio, cure temperature, surfactant
- Advantages relative to gel electrolytes
  - Process base resin without electrolyte
    - Avoid salt contamination effects
    - Prevent evaporation of electrolyte during vacuum / heating
  - Independent selection / engineering of liquid porogen and liquid electrolyte → more design / processing flexibility
  - Minimize likelihood of plasticization of structural polymer

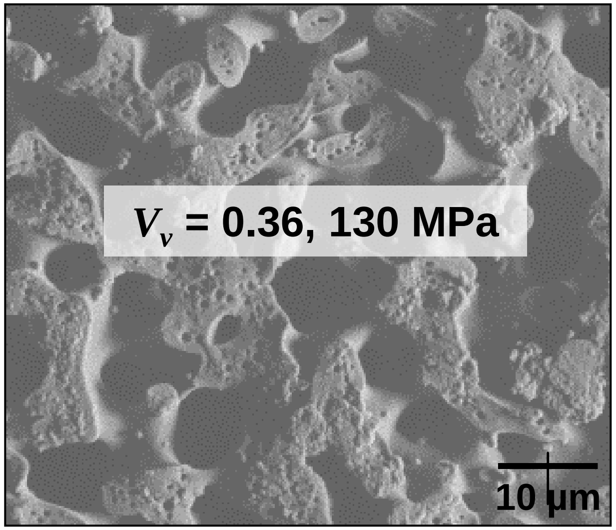
MicroFoam Performance



25% epoxy + 75% PEG



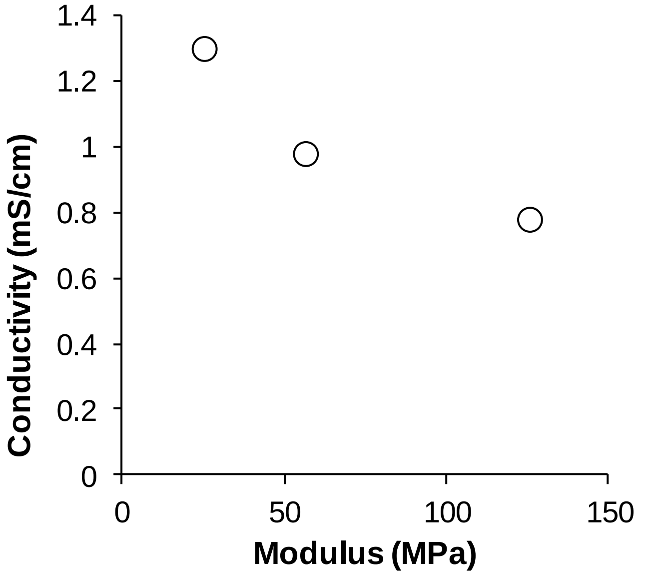
30% epoxy + 70% PEG



35% epoxy + 65% PEG

(all samples: Epon 828 + PACM, 160C cure, 5% PEG-PPG-PEG surfactant, backfilled with 1 M LiTFSI / propylene carbonate electrolyte)

% Epoxy (original mixture)	Void volume fraction	Electrolyte uptake	Conductivity (mS/cm)	Compressive modulus (MPa)
25%	55%	128%	1.3	25.3
30%	51%	105%	0.98	56.5
35%	36%	60%	0.78	125.6

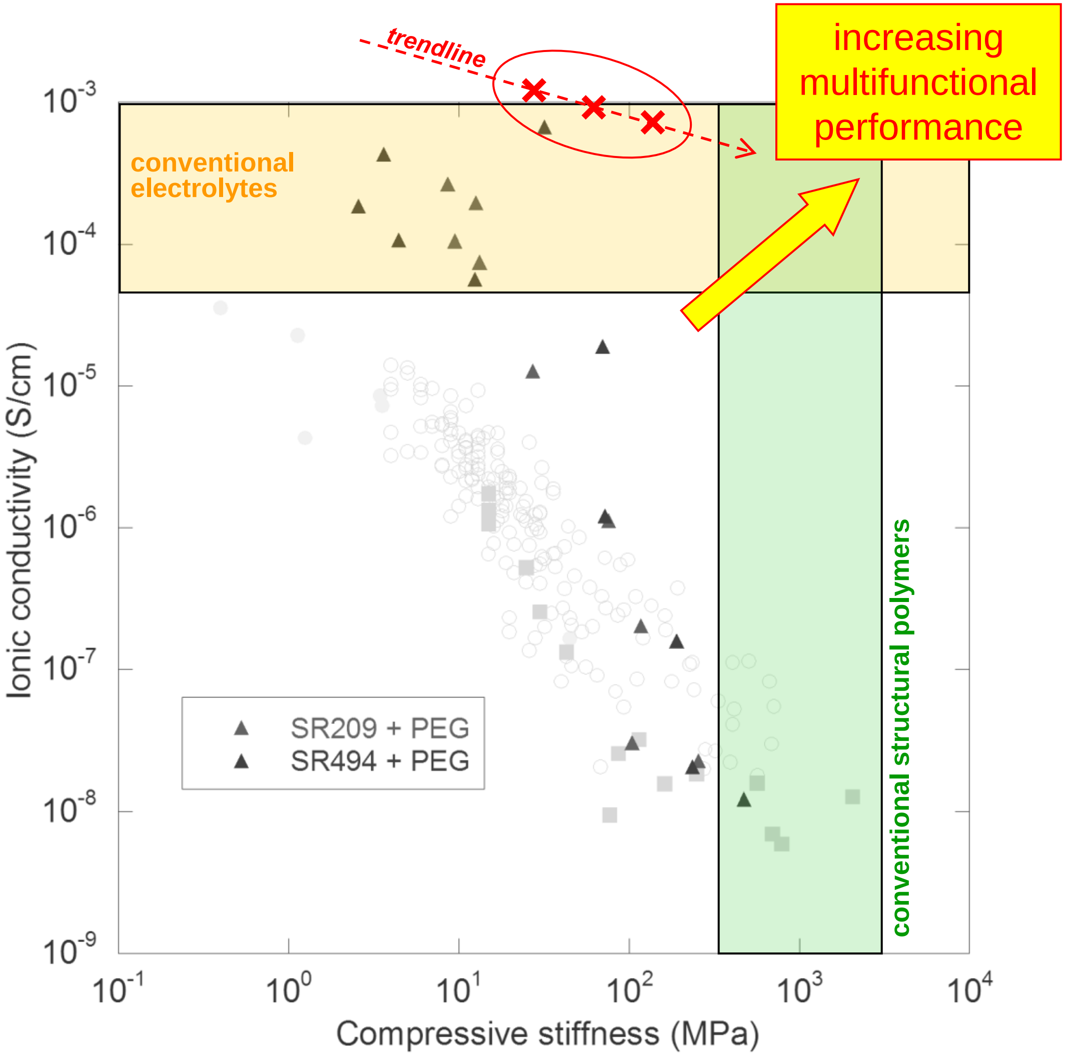


Co-continuous structure (e.g. 35% epoxy) provides best multifunctional performance.

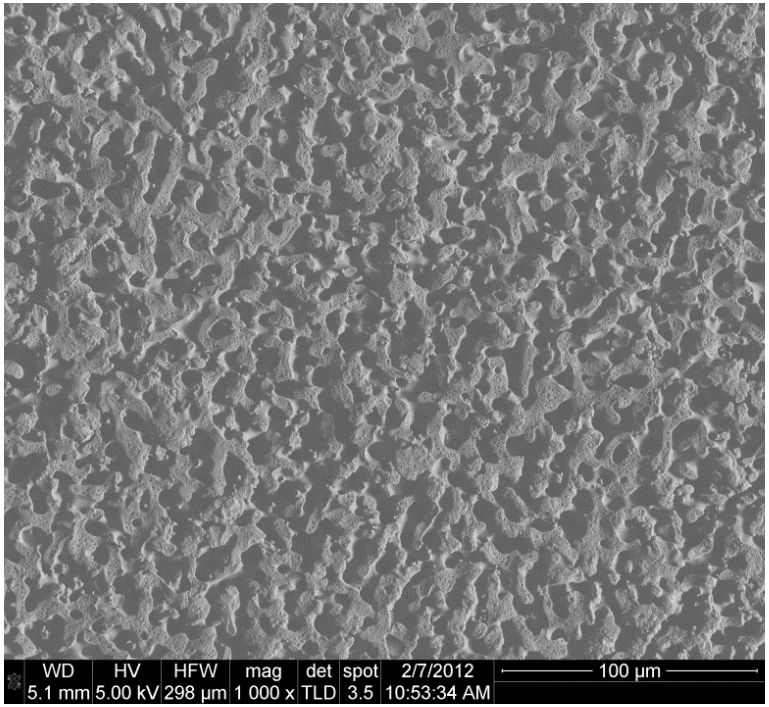
Co-continous structured postulated as idealized multifunctional structures by e.g. Torquato et al. *J. App. Phys.* v94 n9 p5748. 2003.

Multifunctional Properties of MicroFoam Electrolytes

- Microfoam electrolytes provide best multifunctional performance to date → a leading candidate for structural batteries



- Additional processing advantages of microfoam electrolytes are also attractive
- Next challenge → Controlling microstructure near surfaces / interfaces



Conclusions

Technical community is converging towards practical, mass-saving structural power and energy composites.

Continuing Work

- **Capacitors**
  - Continued scaling (lab safety limit $\rightarrow$ 100 J)
  - Beyond commercial FR4 prepreg $\rightarrow$ high dielectric additives, super-clean prepregging

- **Batteries**
  - Further exploration of polymer foam electrolytes
    - Achieve goal of 1 GPa and 0.1 mS/cm
    - Designed, self-assembling electrolyte-electrode interfaces
    - Scaled fabrication
  - Highly structural cathodes
  - Integrated packaging

Effect of Electrode Thickness on Capacitance and Energy Density

$\varepsilon_0 \rightarrow$ permittivity of free space
$\kappa \rightarrow$ matrix relative dielectric constant
$d \rightarrow$ electrode spacing
$h \rightarrow$ electrode waviness amplitude
$l, w \rightarrow$ length, width of unit cell
$C \rightarrow$ capacitance
$\overline{C} \rightarrow$ volume-normalized capacitance
$V \rightarrow$ voltage
$S \rightarrow$ matrix dielectric strength

Thin, Flat Electrode

(e.g. metallized film)

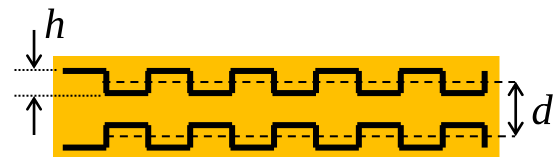
$$C_o = \varepsilon_0 \kappa \frac{lw}{d} \qquad \overline{C}_o = \frac{C_o}{Vol} \rightarrow \boxed{\overline{C}_o = \frac{\varepsilon_0 \kappa}{d^2}}$$

$$\overline{E}_o = \frac{1}{2}\overline{C}_o V^2 = \frac{1}{2}\overline{C}_o (S \cdot d)^2 = \frac{1}{2}\frac{\varepsilon_0 \kappa}{d^2}(S \cdot d)^2$$

$$\boxed{\overline{E}_o = \frac{1}{2}\varepsilon_0 \kappa S^2}$$

Wavy Electrode

(e.g. carbon fabric electrode)



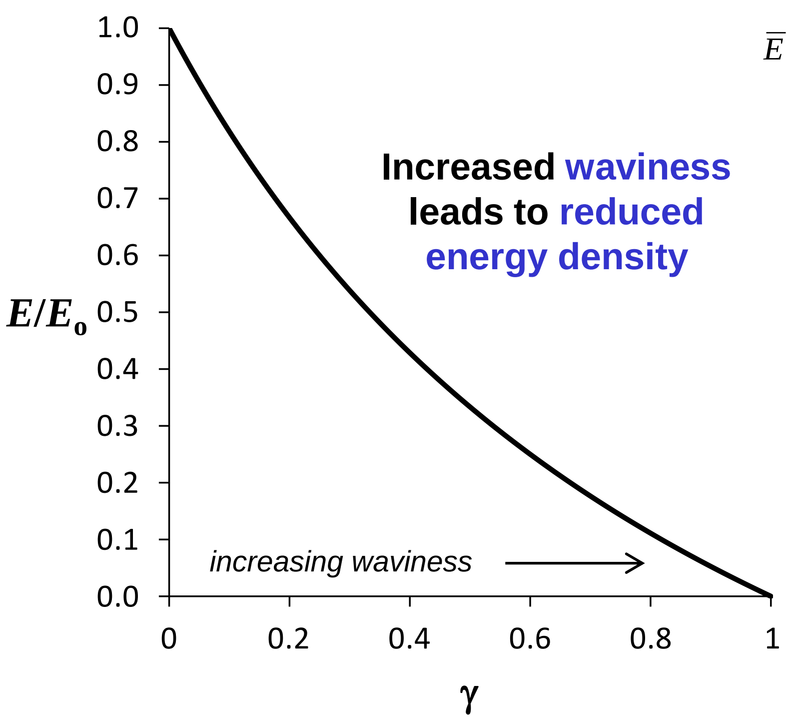
$$\boxed{\gamma \equiv \frac{h}{d}}$$

$$C = \varepsilon_0 \kappa l w \left(\frac{1}{2}\frac{1}{d+h} + \frac{1}{2}\frac{1}{d-h} \right)$$

$$\overline{C} = \frac{C}{Vol} = \frac{\varepsilon_0 \kappa}{d^2}\frac{1}{(1-\gamma^2)} \rightarrow \boxed{\overline{C} = \overline{C}_o \frac{1}{(1-\gamma^2)}}$$

$$\overline{E} = \frac{1}{2}\overline{C}V^2 = \frac{1}{2}\overline{C}(S \cdot (d-h))^2 = \frac{1}{2}\frac{\varepsilon_0 \kappa}{d^2}\frac{1}{(1-\gamma^2)}(S \cdot (d-h))^2$$

$$\overline{E} = \frac{1}{2}\varepsilon_0 \kappa S^2 \frac{(1-\gamma)}{(1+\gamma)} \rightarrow \boxed{\overline{E} = \overline{E}_o \frac{(1-\gamma)}{(1+\gamma)}}$$



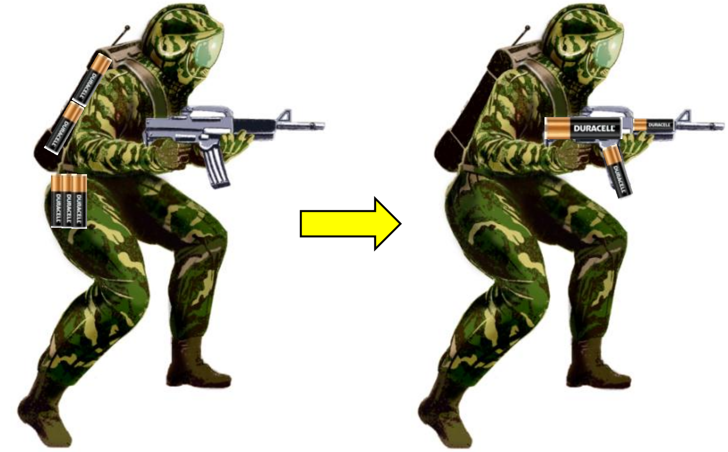
Increased waviness leads to reduced energy density

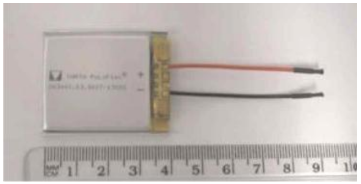
Thin, flat electrodes should be used to achieve maximum energy density.

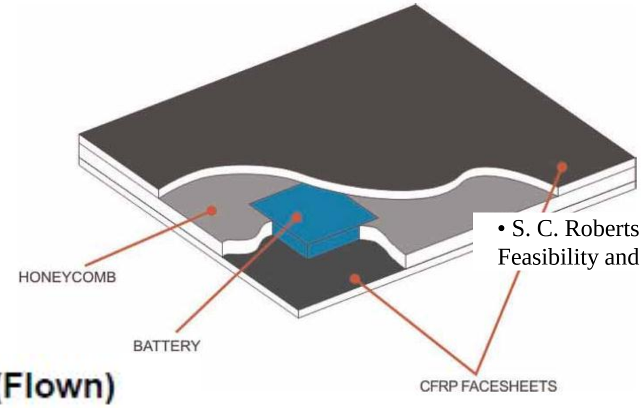
- **In dielectric capacitor, electrodes bus power, but do not store energy → therefore their mass should be minimized**
- **The dielectric body possesses maximum energy when uniformly polarized at limiting dielectric strength → flat electrodes provide uniform electric fields**

One Approach: Embedded Devices

- Battery **packaging used as structure**, or structure used as packaging to **protect / ruggedize battery**
  - **Active battery elements** see **negligible mechanical loads**
- Typical: **embed COTS batteries** into composite structures

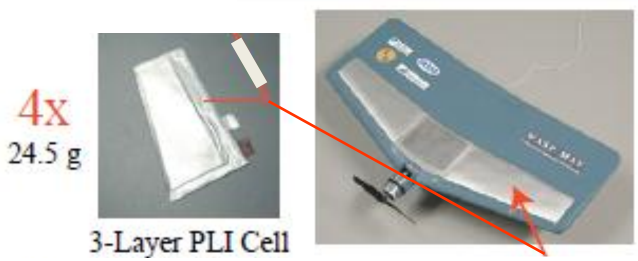




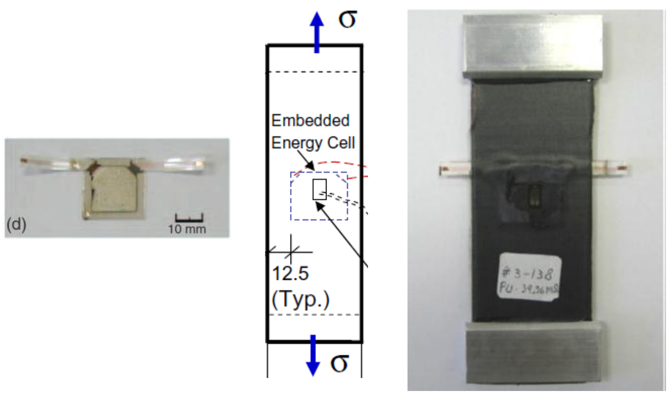


• S. C. Roberts and G. S. Aglietti. "Satellite multifunctional power structure: Feasibility and mass savings." Proc. IMechE. Part G. v222 n1 p41-51. 2008.

PLI Wasp I (Flown)



• J. P. Thomas and M. A. Qidwai. "The design and application of multifunctional structure-battery materials systems." JOM. v57 n3 p18-24. 2005.

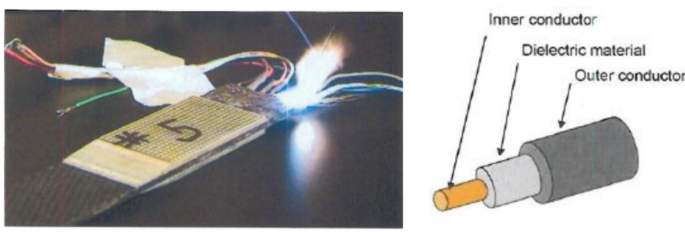


• T. Pereira, Z. Guo, S. Nieh, J. Arias, and H. T. Hahn. "Embedding thin-film lithium energy cells in structural composites." Comp. Sci. Tech. v68 p1935–1941. 2008.

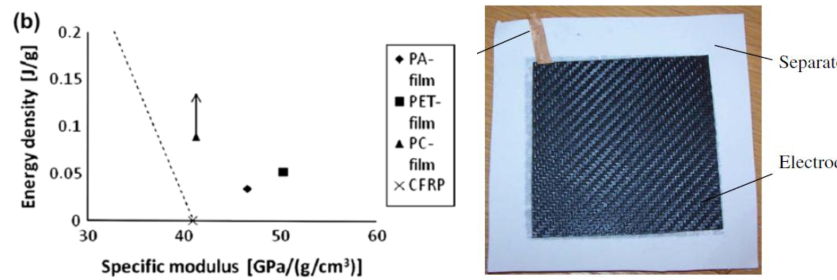
Multifunctional Approach: Structural Devices

J. F. Snyder, D. J. O'Brien, and E. D. Wetzel. "Structural batteries, capacitors, and supercapacitors." Handbook of Solid State Batteries & Capacitors. Eds: N. Dudney, W. West, J. Nanda. To appear.

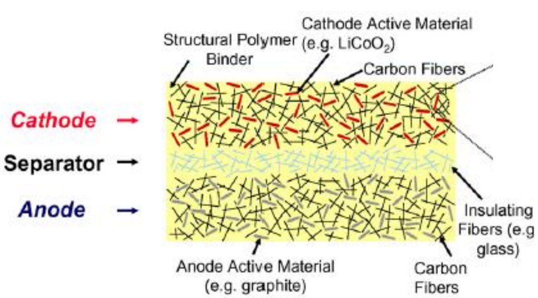
- **Active energy-storing materials directly bear mechanical loads**
  - **Requires development of structural electrolytes, dielectric, electrodes, separators, etc.**
- **Structural capacitors more advanced than structural batteries**



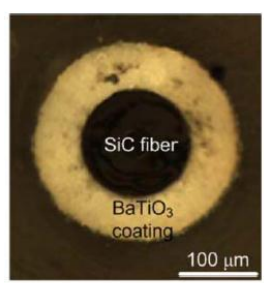
- W. Baron and D. Zeppettella. "Multifunctional airframe structure for energy storage using load bearing coaxial capacitor." Proc. of ASME-SMASIS. SMASIS08-435. 2008.



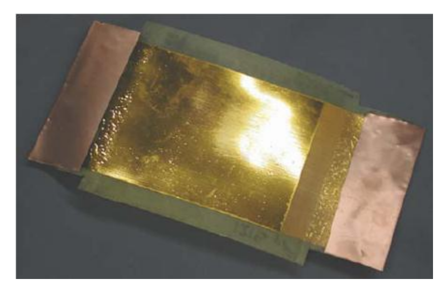
- T. Carlson, D. Ordeus, Maciej Wysocki, and L. E. Asp. "Structural capacitor materials made from carbon fibre epoxy composites." Comp. Sci. Tech. v70 n7 p1135. 2010.



- P. Liu, E. Sherman, and A. Jacobsen. "Design and fabrication of multifunctional structural batteries." J. Power Sources. v189 p646. 2009.



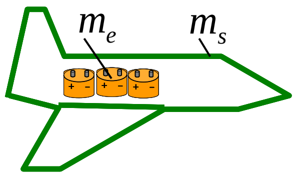
- Y. Lin and H. A. Sodano. "Characterization of multifunctional structural capacitors for embedded energy storage." J. App. Phys. v106 n114108. 2009.



- J. F. Snyder et al. "Structural composite capacitors, supercapacitors, and batteries for U.S. Army applications." Proc. of ASME-SMASIS. SMASIS08-315. 2008.

Mass Savings through Multifunctionality

Conventional design



system mass [kg] — P&E mass [kg] — structure mass [kg]

$$M = m_e + m_s$$

(mass balance)

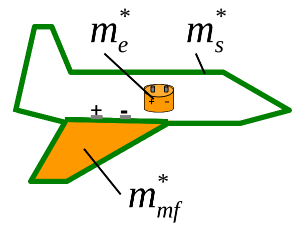
$$\bar{\Gamma} m_e$$

(total system energy capacity)

$$\bar{E} m_s$$

(total system structural capacity)

Multifunctional design



$$M^* = m_e^* + m_s^* + m_{mf}^*$$

structural P&E mass [kg]

(mass balance)

$$\bar{\Gamma} m_e^* + \bar{\Gamma}_{mf} m_{mf}^* = \bar{\Gamma} m_e$$

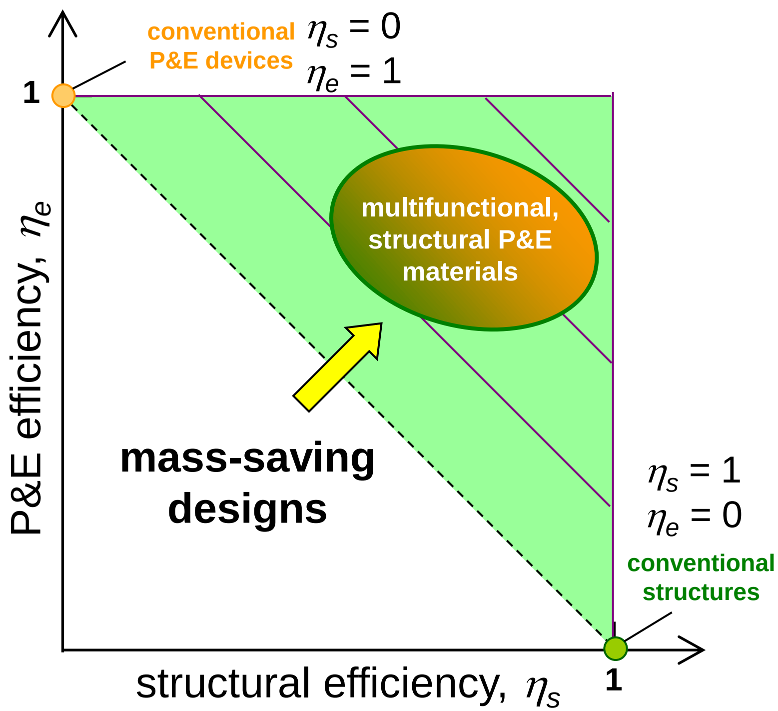
(maintain total system energy capacity)

$$\bar{E} m_s^* + \bar{E}_{mf} m_{mf}^* = \bar{E} m_s$$

(maintain total system structural capacity)

$$\left(M - M^*\right) = \left(\frac{\bar{\Gamma}_{mf}}{\bar{\Gamma}} + \frac{\bar{E}_{mf}}{\bar{E}} - 1\right) m_{mf}^*$$

• D. J. O'Brien, D. M. Baechle, and E. D. Wetzel. "Design and performance of multifunctional structural composite capacitors." *J. Composite Materials*. v45 n26 p2797-2809. 2011.



mass-savings can be achieved if $M^* < M$:

$$\therefore \frac{\bar{\Gamma}_{mf}}{\bar{\Gamma}} + \frac{\bar{E}_{mf}}{\bar{E}} > 1 \quad \Rightarrow \quad \boxed{\eta_{mf} \equiv \eta_e + \eta_s > 1}$$

$$\eta_e = \frac{\bar{\Gamma}_{mf}}{\bar{\Gamma}} = \frac{\text{energy density of multifunctional structure}}{\text{energy density of conventional P\&E}}$$

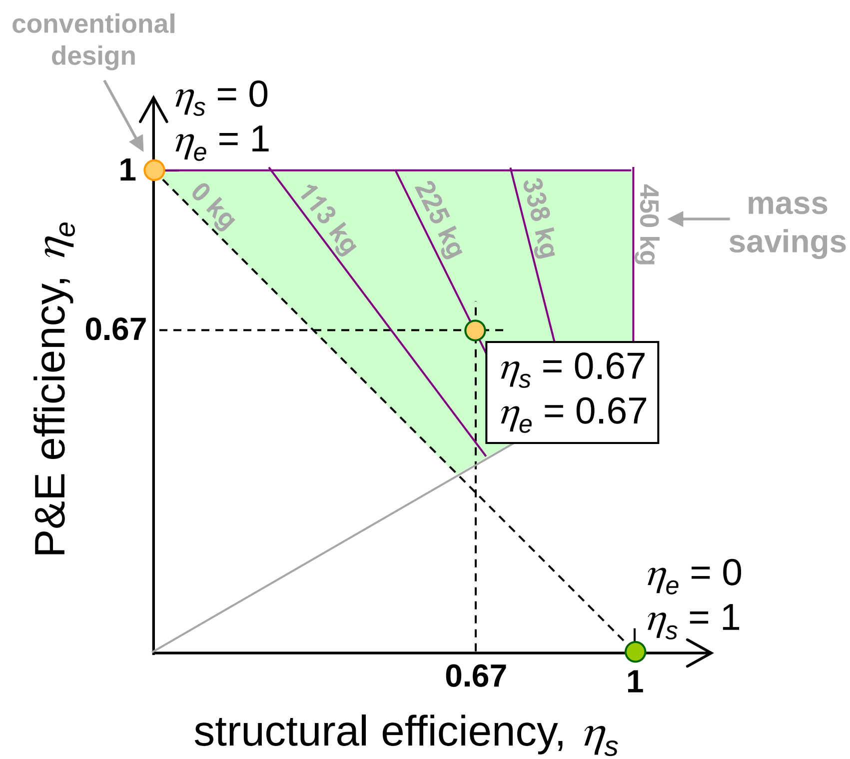
$$\eta_s = \frac{\bar{E}_{mf}}{\bar{E}} = \frac{\text{specific stiffness of multifunctional structure}}{\text{specific stiffness of conventional structure}}$$

Mass savings possible even if multifunctional material performs individual functions less efficiently than monofunctional materials.

Example: Commercial Electric Automobile

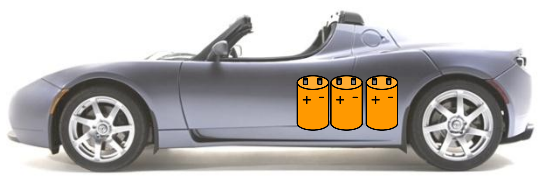
Prius : 21 kW, 202V, 45kg NiMH battery pack, 1300 kg curb weight

Tesla Roadster: 215 kW, 375 V, 450 kg Li-ion battery pack, 1220 kg curb weight



Conventional design

	770 kg structure	($\eta_e = 0$, $\eta_s = 1$)
+	450 kg battery	($\eta_e = 1$, $\eta_s = 0$)
	1220 kg total system weight	



Multifunctional design

	320 kg structure	($\eta_e = 0$, $\eta_s = 1$)
+	675 kg structural battery	($\eta_e = 0.67$, $\eta_s = 0.67$)
	995 kg total system weight	

System weight reduced by 18%

Underside of the Tesla Roadster's carbon fiber rear panel.

Tesla roadster uses RTM-ed, epoxy carbon fiber composite body panels with a glass fiber / polypropylene interlayer.